

PATENT SPECIFICATION

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(54) CROSS-LINKING PROCESS

(71) We, DOW CORNING LIMITED, a British Company, of 12 Whitehall, London, SW1A 2DZ, do hereby declare the invention for which we pray that a Patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

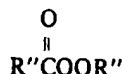
This invention relates to a process for effecting cross-linking in polyethylene and copolymers of ethylene with other vinylic monomers. The invention also relates to cross-linked polyethylene and copolymers whenever prepared by the said process.

It is known from U.K. Patent No. 1,286,460 that polyethylene and certain copolymers of ethylene may be cross-linked by (A) reacting the polyethylene or copolymer with a defined silane in the presence of a compound capable of generating radical sites in the polyethylene, and (B) exposing the product of (A) to water in the presence of a silanol condensation catalyst. By means of said process it is possible to produce cross-linkable polyethylene or copolymer which is useful in the fabrication of, for example, pipe, electrical insulation and film, and after fabrication to cross-link the product.

According to the disclosure in Patent No. 1,286,460 the preferred radical generating compounds for use in said process are the organic peroxides and peresters, with dicumyl peroxide being particularly preferred. The use of peroxides and peresters such as benzoyl peroxide, dicumyl peroxide and tertiary-butyl perbenzoate, however, is not entirely satisfactory. When said peroxy compounds are employed, it has been found that during Step (A) of the process the melt index of the polyethylene or copolymer decreases. If the polyethylene or copolymer has a low initial melt index the product resulting after the application of Step (A) is often difficult to shape by extrusion. Consequently, where the cross-linkable product is to be extruded it has been found desirable to employ an injection moulding grade of polyethylene or copolymer, having a higher initial melt index, rather than an extrusion grade.

We have now discovered that the above mentioned change in melt index can be reduced if there are employed during Step (A) of the process certain specified freed radical generating compounds.

Accordingly this invention provides a process for effecting cross-linking in a polyolefin, which is polyethylene, a copolymer of ethylene with up to 10 molar percent of one or more of propylene, butene-1 and hexene-1, or a copolymer of ethylene with up to 50 molar percent of vinyl acetate or ethyl acrylate, which comprises (A) reacting said polyolefin with a silane of the general formula $RR'SiY_2$ in which R represents a monovalent olefinically unsaturated radical attached to silicon through a silicon to carbon bond and composed of carbon, hydrogen and, optionally, oxygen, each Y represents a hydrolysable organic radical and R' represents a monovalent hydrocarbon radical free of aliphatic unsaturation or a hydrolysable organic radical, in the presence of a free radical generating compound which is a compound of the general formula



in which R'' represents a secondary or tertiary alkyl radical, a cycloalkyl radical

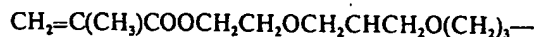
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having more than 4 carbon atoms or a benzyl radical and R''' represents a tertiary alkyl radical or a cumyl radical, said reaction being performed at a temperature at which the free radical generating compound has a half-life of less than 6 minutes, and (B) subsequently exposing the product of (A) to water in the presence of a silanol condensation catalyst.

The polyolefins to which the process of this invention may be advantageously applied are polyethylene, copolymers of ethylene with up to 10 molar percent, preferably from 1 to 5 molar percent, with one or more of propylene, butene-1 and hexene-1 and copolymers of ethylene with up to 50 molar percent of vinyl acetate or ethyl acrylate. In view of their widespread commercial usage, the invention is of particular interest with respect to the cross-linking of ethylene homopolymers or copolymers of ethylene with a few per cent of propylene, butene-1 or hexene-1.

In the general formula of the silanes employed in the process of this invention, R represents a monovalent olefinically-unsaturated radical composed of carbon, hydrogen and, optionally, oxygen. Examples of such radicals are vinyl, allyl, butenyl, cyclohexenyl, cyclopentadienyl, cyclohexadienyl, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3-$, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{O}(\text{CH}_2)_3-$ and

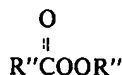
OH



the vinyl radical being preferred. The group Y may represent any hydrolysable organic radical, for example an alkoxy or alkoxyalkoxy radical, such as the methoxy, ethoxy, butoxy and methoxyethoxy radicals, an acyloxy radical, for example the formyloxy, acetoxy or propionoxy radicals, an oximo radical e.g. $-\text{ON}=\text{C}(\text{CH}_3)_2$, $-\text{O}=\text{CHCH}_2\text{C}_6\text{H}_5$ and $-\text{ON}=\text{C}(\text{C}_6\text{H}_5)_2$ or a substituted amino radical e.g. alkylamino and arylamino radicals, examples of which are $-\text{NHCH}_3$, $-\text{NHC}_2\text{H}_5$ and $-\text{NH}(\text{C}_6\text{H}_5)$. Preferably each Y represents an alkoxy or alkoxyalkoxy radical having from 1 to 4 inclusive carbon atoms. The group R' may represent a monovalent hydrocarbon radical free of aliphatic unsaturation e.g. methyl, ethyl, propyl, tetradecyl, octadecyl, phenyl, benzyl or tolyl. It may also represent a hydrolysable organic group. The preferred silanes are those having the formula $\text{R}'\text{SiY}_3$, the most preferred silanes being vinyl trimethoxysilane, vinyl triethoxysilane and vinyl tris(methoxyethoxy)silane. Silanes having only two hydrolysable groups e.g. vinyl methyldiethoxysilane and vinyl phenyldimethoxysilane, are, however, also operative.

The proportion of silane employed will depend in part upon the reaction conditions and in part on the degree of cross-linking desired in the polyolefin. The actual proportion may vary widely, for example from 0.1 to 20 percent by weight based on the weight of polyolefin. In general, however, we prefer to employ from 0.5 to 5 per cent by weight based on the weight of the polyolefin.

As the free radical generating compound there is employed a compound of the general formula



in which R'' represents a secondary or tertiary alkyl radical, a cycloalkyl radical having more than 4 carbon atoms or a benzyl radical and R''' represents a tertiary alkyl radical or a cumyl radical. The preferred R'' radicals are those having less than 18 carbon atoms for example isopropyl, t-butyl, t-pentyl, cyclohexyl and sec-hexyl, the tertiary radicals e.g. t-butyl being most preferred. Preferably R''' has less than 12 carbon atoms and most preferably R''' is t-butyl. Specific compounds which are included within the scope of the general formula are tert-butyl perphenylacetate, tert-butyl perisobutyrate, tert-butyl per(sec)octoate, tert-butyl perpivalate, cumyl perpivalate and t-butyl perdiethylacetate.

The reaction is believed to proceed by the generation of radical sites in the polyolefin by the free radical generating compound leading to grafting of the silane to the polyolefin. Sufficient of the free radical generating compound should be employed to obtain the desired degree of reaction of the silane with the polyolefin.

The proportion of free radical generating compound may vary from as little as 0.01 per cent by weight up to 2 or 3 per cent by weight based on the weight of the polyolefin. Where the maximum degree of cross-linking is desired in the final product we prefer to employ at least 0.25% and up to 1.5% by weight of the free radical generating compound.

The particular free radical generating compound chosen in any particular instance will depend on the temperature at which the reaction between the silane and the polyolefin is to be performed. At the lower reaction temperatures a free radical generating compound having an appropriately short half life at that temperature should be used. The half life of the compound at the reaction temperature should be less than 6 minutes and preferably less than 2 minutes.

The reaction according to Step (A) may be performed at any temperature above the melting point of the polyolefin to just below the temperature at which significant degradation of the polyolefin occurs. When the polyolefin is polyethylene the reaction is preferably performed at a temperature in the range from 115°C up to 250°C. Temperatures as low as 80°C. may however be used depending on the type of polyolefin.

The reaction may be performed employing any suitable apparatus. Preferably, the reaction is carried forward under conditions in which the copolymer is subjected to mechanical working. The reaction is therefore preferably carried out in, for example, an extruder of an internal Banbury mixer provided it is adapted to permit the copolymer to reach the desired temperature. A preferred form of apparatus is that of the type which comprises a closed extruder adapted to effect a kneading or compounding action on its contents. A commercially available apparatus of this type is that known as the Ko-Kneader which is capable of effecting the mechanical working and compounding of plastics at elevated temperatures. The Ko-Kneader also generally includes a vacuum port which may be employed to remove any unreacted silane.

The polyolefin and silane reactants may be brought together by any convenient means. For example the liquid silane may be introduced into the apparatus in which the reaction is to take place dispersed on the surface of the polyolefin, or it may be metered directly into the apparatus. The free radical generating compound may also be introduced by way of the surface of the polyolefin or may be added, solubility considerations permitting, as a solution in the silane.

Minor amounts of organic solvents may be employed, if desired, to facilitate the addition of the free radical generator or the silane. However, the reaction is usually best carried out in the absence of added solvents as this avoids subsequent solvent removal procedures or contamination of the product.

Cross-linking of the silane-modified polyolefin according to Step (B) of the process of this invention is effected by exposing the product of Step (A), usually after shaping by extrusion or other processes, to water in the presence of a silanol condensation catalyst. The moisture present in the atmosphere is usually sufficient to permit cross-linking to occur but the rate of cross-linking may be hastened if desired by the use of an artificially moistened atmosphere or immersion in liquid water, optionally employing elevated temperatures. Preferably cross-linking is effected at a temperature between 50°C and 100°C.

Provided the reaction product of the polyolefin and the silane is kept free of moisture and/or of material which acts as a silanol condensation catalyst, it may be stored, if desired, prior to the application of Step (B). As it is often difficult to exclude all traces of moisture from the copolymer the preparation of a product which remains stable over a long period with respect to further cross-linking is usually only possible when the hydrolysable moieties in the silane are those, such as alkoxy radicals, which give rise to non-catalytic by-products. When the silane contains, for example, silicon-bonded acetoxy radicals or even trace quantities of silicon-bonded chlorine atoms the acetic acid or hydrochloric acid by-products can cause some cross-linking to occur at normal ambient temperatures if moisture has not been excluded from the composition.

If a storage stable product is not desired the use of a silane of other additive which generates a silanol condensation catalyst in situ during hydrolysis may be permissible, or even preferred. In general, however, we prefer to incorporate the silanol condensation catalyst into the product of Step (A) only when it is desired to effect cross-linking of the product, for example, just prior to shaping into the finished article. Thus Step (A), the addition of the silanol condensation catalyst and shaping of the cross-linkable product may take place continuously, for

example by performing all of these operations in a single compounding extruder. Alternatively the cross-linkable polyolefin compositions can be provided in the form of two separate components, one component comprising the polyolefin which has been modified according to Step (A), the other component comprising a composition obtained by mixing the silanol condensation catalyst with polyolefin which has not been modified by reaction with the silane. The two components may then be blended in the desired proportions to provide a composition which is cross-linkable in the presence of water. If a polyolefin having the maximum degree of cross-linking capability is required any unmodified polyolefin included in the composition is kept to a minimum and preferably comprises not more than 10 per cent by weight of the total quantity of the polyolefin in the mixed composition. When preparing a cross-linkable polyolefin by this technique we prefer to employ from 1 to 10 per cent by weight of the unmodified copolymer catalyst component based on the total polyolefin content of the composition. Preferably also, the polyolefin used in the catalyst component has flow characteristics which are the same as, or approximate to that of the silane-modified copolymer with which it is to be mixed.

Any of the wide variety of materials which function as silanol condensation catalysts may be employed in the process of this invention. Such materials include, for example, metal carboxylates such as dibutyltin dilaurate, stannous acetate, stannous octoate, lead naphthenate, zinc octoate, iron-2-ethylhexoate and cobalt naphthenate, organic metal compounds such as the titanium esters and chelates, for example tetrabutyl titanate, tetranonyl titanate and bis(acetylacetonyl-di-propyl titanate, organic bases such as ethylamine, hexylamine, dibutylamine and piperidine and acids such as the mineral acids and fatty acids. The preferred catalysts are the organic tin compounds, particularly the tin carboxylates, for example dibutyltin dilaurate, dibutyltin diacetate and dibutyltin dioctoate.

Having regard to the considerations discussed hereinabove the silanol condensation catalyst may be incorporated prior to, during, or following the reaction of the polyolefin and the silane. The catalyst may be added as such or generated *in situ* either by hydrolysis of the silane or, for example, by the thermal decomposition of a material which liberates an amine or other silanol condensation catalyst as a decomposition product.

A further method of employing the catalyst which may be used is described in our co-pending application No. 52548/71 (Serial No. 1,357,549) and comprises contacting the silane-modified polyolefin with an aqueous dispersion or solution of an organic tin compound.

In addition to the presence of the silanol condensation catalyst or precursor thereof the polyolefin may contain, if desired, other ingredients, for example oxidation inhibitors, fillers and pigments. Polyolefin modified according to Step (A) may also be blended with unmodified polyolefin or other type of polymer.

Cross-linked polyolefins produced according to the present invention possess improved strength at elevated temperature when compared with the uncross-linked polyolefins. They may be employed in a variety of applications, for example as electrical insulation, plastic foam and in the fabrication of pipes and containers. The process is of particular applicability with regard to the provision of extruded articles. By means of this invention the reduction in melt index which can take place during the reaction between the polyolefin and the silane is minimised. The process of the invention is therefore particularly adapted to effecting the cross-linking of polyolefins having an initial melt index of less than 2.0 g./10 min. It enables the tough, high molecular weight polyolefins to be employed in the fabrication of cross-linked extruded and injection moulded articles.

It has also been found that the use of the specified peroxy compounds according to the invention enables production of tough cross-linked polyolefin film having less imperfections ("fish eyes") than that obtained when, for example, dicumyl peroxide is employed as the radical generating compound.

The following examples in which the parts are expressed by weight illustrate the invention. In the examples the gel content refers to the percentage insoluble material in the polymer. It was determined by placing a sample of the polymer weighing 0.75 g. in refluxing xylene for 20 hours. The remaining portion (if any) was then recovered, weighed and its weight expressed as percentage of the weight of the original sample.

The melt index values referred to herein are those measured according to the procedure of British Standard Specification No. 2782 (1956), Method 105C.

Example 1.

100 parts of a granular general purpose low density polyethylene (Carlona, grade 18—003 GB) (Carlona is a Registered Trade Mark), having a melt index of 0.28 g./10 min. and nominal density of 0.918 g./cc., were coated by tumbling with 2 parts of vinyltrimethoxysilane having dissolved therein 0.75 parts of t-butyl perpivalate until all of the liquid had been taken up. The composition was then extruded using a PR46 Buss Ko-Kneader using the following conditions:

Temperature of screw: Neutral

Temperature of barrel zone 1 125°C

10 " " " " 2 " 10
 " " crosshead
 extruder "

Output: 115 g./min.

The extrudate was cut into pieces on emergence from the extruder and the pieces cooled by momentary contact with water (face-cutting).

The procedure was then repeated several times varying the proportions of t-butyl perpivalate and the processing conditions as shown in the Table. The recovered extrudates (C) were each free of gel, that is cross-linked matter, as measured after immersion in refluxing xylene for 20 hours. The melt index was measured for each extrudate.

A composition (D) was then prepared using 100 parts of an injection moulding grade low density polyethylene (Carlona 25—020MA) in granule form and 0.25 parts of dibutyltin dilaurate. Extrusion at 135°C and granulation yielded a product having an unchanged melt index.

95 parts of the extrudates (C) were each mixed with 5 parts by weight of (D) by dry tumbling for 20 minutes to give several cross-linkable compositions. These compositions were separately extruded using the Buss Ko-Kneader at 135°C and moulded into sheets of thickness 0.125 inch. The sheets were then cross-linked by immersion in water at 100°C for 24 hours. After this time the proportion of insoluble gel in each sample, i.e. the gel content, was measured. The values of the melt index and gel content obtained for the various samples are shown in the following table.

Run	Temp. of Barrel °C	Output of PR 46 g./min.	Parts of t-Butyl perpivalate	Melt Index of Extrudate g./10 min.	Gel Content %
1	125	115	0.75	0.14	66.5
2	160	150	0.50	0.15	62.5
3	160	140	0.75	0.15	66.3
4	200	140	0.50	0.16	68.0
5	200	150	0.75	0.13	72.0

When Run 4 was repeated employing 0.20 parts of dicumyl peroxide in an extrudate having a melt index of less than 0.01 was obtained.

Example 2.

100 parts of low density polyethylene granules (XNM 68) having a melt index of 6.9 g./10 min. and nominal density of 0.923 g./cc. were coated by tumbling with 2 parts of vinyltrimethoxysilane containing 0.75 parts of t-butyl perpivalate. The composition was then extruded on a PR 46 Buss Ko-Kneader with the cross head extruder fitted and using the following conditions:

Temperature of screw	Neutral
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„	„ barrel Zone 1	200°C
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„	„ „ „ 2	200°C
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„	„ cross head extruder barrel	200°C
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Output: 165 g./min.

The extrudate was cut into pieces on emergence from the Ko-Kneader and the pieces cooled by momentary contact with water (face-cutting).

The recovered extrudate contained no gel and had a melt index of 6.5. The extrudate was mixed with 0.0125% by weight of dibutyltin dilaurate using the same procedure as in Example 1 and exposed as 0.125 inch thick plates to water at 100°C for 24 hours. The resulting product had a gel content of 60.2%.

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When the first step of the above procedure was repeated employing 0.25 part of dicumyl peroxide in place of the t-butyl perpivalate an extrudate was obtained having a melt index of 0.25 g./10 min.

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Example 3.

95 parts of the product of run 5 in Example 1 was tumble mixed with 5 parts of component D in Example 1 and extruded at 200°C on a BTL one inch Titan (Registered Trade Mark) extruder to make a thin film (thickness approximately 0.03 mm.). This film was substantially free of infusible particles and after immersion in water at 100°C for 24 hours had a gel content of 72%.

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Example 4.

100 parts of low density polyethylene granules (Carlona grade 18—003 GB), having a melt index of 0.28 g./10 min. and nominal density of 0.918 g./cc. were coated by tumbling with 2 parts of vinyltrimethoxysilane containing 0.5 parts t-butyl per(sec)octoate. The composition was then extruded on a PR 46 Buss Ko-Kneader with the cross head extruder fitted and using the following conditions:

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Temperature of screw	Neutral
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„	„ barrel Zone 1	200°C
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„	„ „ Zone 2	200°C
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„	„ cross head extruder barrel	200°C
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Output: 125 g./min.

The extrudate was cut into pieces on emergence from the extruder and the pieces cooled by momentary contact with water (face-cutting).

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The recovered extrudate contained no gel and had a melt index of 0.1 g./10 min. It was mixed with 0.0125% by weight of dibutyltin dilaurate using the same procedure as in Example 1 and exposed as a 0.125 inch thick plate to water at 100°C for 24 hours. The resulting product had a gel content of 77%.

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Example 5.

100 Parts of ethylene-vinyl acetate copolymer (Elvax 150) (Elvax is a Registered Trade Mark) containing approximately 33 mole % of units derived from vinyl acetate and having a melt flow index of approximately 40 was reacted with 2 parts of vinyl trimethoxysilane and 0.75 parts of t-butyl perpivalate using the general technique described in the preceding examples. The screw temperature of the Ko-Kneader was 170°C and the output 100 g./min.

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The product (M.I.=16 g./10 min.) was granulated, pressed into sheets of 3 mm. thickness and the sheets immersed for 20 hours in a 5% by weight emulsion of dibutyltin dilaurate maintained at 80°C. The resulting product had a gel content of 80%.

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Example 6.

Employing the procedure and conditions of Example 2, 100 parts of

polyethylene granules (XNM 68) having a melt index of 8.1 g./10 min. and density of 0.923 g./cc. were reacted with 2 parts of vinyl trimethoxysilane and 0.5 part of t-butyl perdiethylacetate $(CH_3)_2CHCO.O-OC(CH_3)_3$. The resulting extrudate contained no gel and had a melt of 4.4 g./10 min. It was exposed, as a rod of 3 cm. diameter to a 0.2% by weight aqueous emulsion of dibutyltin dilaurate at 100°C for 20 hours. The resulting product had a gel content of 64%.

Example 7.

The procedure of Example 6 was repeated employing 0.5 part of t-butyl perisobutyrate $(CH_3)_2CHCO.O-OC(CH_3)_3$ in place of the t-butyl perdiethylacetate. The resulting extrudate contained no gel and had a melt index of 4.3 g./10 min. After exposure to the dibutyltin dilaurate emulsion the product had a gel content of 66%.

Example 8.

The procedure of Example 6 was repeated using as the polyethylene 100 parts of Carlona 18A 20FA (M.I.=2.1 g./10 min., density=0.918 g./cc.) and 0.5 parts of cumyl perpivalate $(CH_3)_2CCO.O-OC(CH_3)_2(C_6H_5)$ as the free radical generator. The recovered extrudate contained no gel and had a melt index of 1.2 g./10 min. After exposure to the aqueous dibutyltin dilaurate emulsion the product had a gel content of 60%.

Example 9.

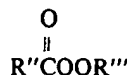
The procedure of Example 6 was employed to react 100 parts of a high density polyethylene (Stamylan 9300, M.I.=7.5 g./10 min., density=0.965 g./cc.), with 2 parts of vinyl trimethoxysilane containing 0.75 parts of t-butyl perpivalate. The temperature employed in the extruder barrel was 235°C. and the output was 180 g./min.

The recovered extrudate contained no gel and had a melt index of 5.0 g./10 min.

After immersion of the extrudate (as rods of 3 mm. diameter) in a 0.2% w/w aqueous emulsion of dibutyltin dilaurate at 100°C for 20 hours the resulting product had a gel content of 57%.

WHAT WE CLAIM IS:—

1. A process for effecting cross-linking in a polyolefin which is polyethylene, a copolymer of ethylene with up to 10 molar percent of one or more of propylene, butene-1 and hexene-1, or a copolymer of ethylene with up to 50 molar percent of vinyl acetate or ethyl acrylate, which comprises (A) reacting said polyolefin with a silane of the general formula $RR'SiY$ in which R represents a monovalent olefinically unsaturated radical attached to silicon through a silicon to carbon bond and composed of carbon, hydrogen and, optionally, oxygen, each Y represents a hydrolysable organic radical and R' represents a monovalent hydrocarbon radical free of aliphatic unsaturation or a hydrolysable organic radical, in the presence of a free radical generating compound which is a compound of the general formula



in which R'' represents a secondary or tertiary alkyl radical, a cycloalkyl radical having more than 4 carbon atoms or a benzyl radical and R''' represents a tertiary alkyl radical or a cumyl radical, said reaction being performed at a temperature at which the free radical generating compound has a half-life of less than 6 minutes, and (B) subsequently exposing the product of (A) to water in the presence of a silanol condensation catalyst.

2. A process as claimed in claim 1 wherein the silane is one or more of vinyl trimethoxysilane, vinyl triethoxysilane and vinyl tris(methoxyethoxy)silane.

3. A process as claimed in claim 1 or claim 2 wherein the silane is employed in a proportion of from 0.5 to 5% by weight based on the weight of the polyolefin.

4. A process as claimed in any one of the preceding claims wherein in the general formula R'' represents the tertiary butyl radical.

5. A process as claimed in any one of the preceding claims wherein R''' represents the tertiary butyl radical.

6. A process as claimed in any one of the preceding claims wherein the free radical generating compound has a half life of less than 2 minutes at the reaction temperature.

7. A process as claimed in any one of the preceding claims wherein the free radical generating compound is employed in a proportion of from 0.25 to 1.5% by weight of polyolefin.

8. A process as claimed in any one of the preceding claims wherein the polyolefin is polyethylene and the reaction between the silane and the polyethylene is effected at a temperature within the range from 115 to 250°C.

9. A process as claimed in any one of the preceding claims wherein step (A) is carried out under conditions in which the polyolefin is subjected to mechanical working.

10. A process as claimed in claim 9 wherein step (A) is carried out in an extruder adapted to effect a kneading or compounding action on its contents.

11. A process as claimed in any one of the preceding claims wherein the silanol condensation is a tin carboxylate.

12. A process as claimed in any one of the preceding claims wherein subsequent to step (A) the product therefrom is blended with the said silanol condensation catalyst and thereafter formed into a shaped article prior to effecting step (B).

13. A process for effecting cross-linking in a polyolefin as claimed in claim 1 substantially as described with reference to Examples 1 to 4 inclusive.

14. A process for effecting cross-linking in a polyolefin as claimed in claim 1 substantially as described with reference to Examples 5 to 9 inclusive.

15. A process for effecting cross-linking in a polyolefin which is polyethylene, a copolymer of ethylene with up to 10 molar per cent of one or more of propylene, butene-1 and hexane-1, or a copolymer of ethylene with up to 50 per cent of vinyl acetate or ethyl acrylate, which comprises exposing to water in the presence of a silanol condensation catalyst a polyolefin which has been modified by reaction with a silane as specified in step (A) of any of the preceding claims.

16. A cross-linked polyolefin or shaped article thereof whenever obtained by the process claimed in any one of the preceding claims.

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